other VOC are removed. The bottoms from the organic absorber (Stream 6) flow to the HCl stripper for recovery of HCl. The overhead gas (Stream 5) is sent to HCl absorption. By-product HCl is then removed in the HCl absorber, where it is saturated by washing with a refrigerated solvent (e.g., o-DCB) or low vapor pressure oil, and then recovered in wash towers as commercially usable hydrochloric acid.<sup>98</sup>

Crude reaction liquid product (Stream 4) enters the crude chlorobenzene distillation column, which produces overheads (Stream 7) that contains most of the chlorobenzenes, unreacted benzene, and some HCl, and a bottom stream from which catalyst and other byproducts are separated (Stream 8) and processed for reuse. The overheads (Stream 7) pass through an HCl stripper and into a benzene recovery column (Stream 9). Part of the subsequent benzene-free stream (Stream 10) is returned to the organic absorber; the remainder (Stream 11) enters the MCB distillation column. The overhead MCB distillation product (Stream 12) is then stored and the bottom stream containing DCB and TCB isomers is processed.<sup>98</sup>

Figure 5-14 presents basic operations that may be used to produce o- and p-DCB and TCB. In a continuation of the production of MCB, o- and p-DCB can be separated by fractional distillation. Isomer fractionation yields p-DCB (with traces of o-DCB and m-DCB), which enters the overhead (Stream 1); the o-DCB enters the bottoms (Stream 2). The o-DCB bottoms (Stream 2) undergoes fractional distillation and produces an o-DCB overhead (Stream 3), which is sent to storage, and bottoms (Stream 4), which is further processed to yield TCBs. 98

The crude p-DCB with other trace isomers (Stream 5) is purified by batch crystallization. Part of the purified p-DCB (Stream 6) is sent to liquid storage. The remainder (Stream 7) undergoes freezing, crushing, screening, and packing of p-DCB crystals. The mother liquor from crystallization (Stream 8) is sent to DCB solvent-grade fractionalization, where it is separated into solvent grade o-DCB (Stream 9) and p-DCB (Stream 10) and stored.<sup>98</sup>

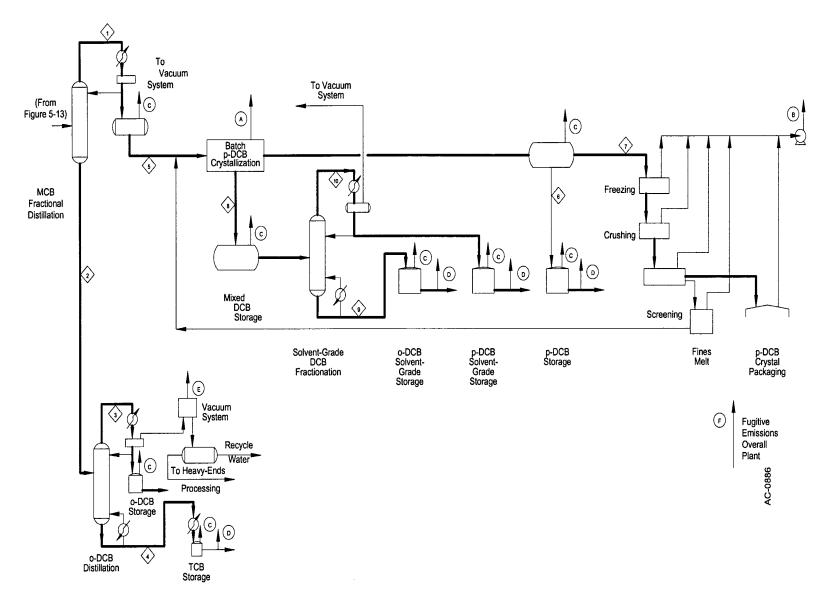


Figure 5-14. Dichlorobenzene and Trichlorobenzene Continuous Production Diagram

Source: Reference 19.

The isolation of m-DCB from mixed DCB streams is not economical, because it usually occurs at a level of 1 percent or less. Metadichlorobenzene is sold with other isomers as mixed chlorobenzenes.<sup>98</sup>

Other processes that are most often used in the production of MCB are the batch and Rashing methods. Other TCB production processes are the reaction of  $\alpha$ ,  $\beta$ , or  $\gamma$ -benzene hexachloride with alcoholic potash, the dehalogenation of  $\alpha$ -benzene hexachloride with pyridine, and the reaction of  $\alpha$ -benzene hexachloride with calcium hydroxide to form primarily 1,2,4-TCB. On the production of  $\alpha$ -benzene hexachloride with calcium hydroxide to form primarily 1,2,4-TCB.

## 5.7.2 <u>Benzene Emissions from Chlorobenzene Production</u>

The primary source of benzene emissions during MCB production is the tail gas treatment vent of the tail gas scrubber (Vent A in Figure 5-13). Usually, this vent does not have a control device.<sup>19</sup> Other potential sources of benzene emissions are atmospheric distillation vents from the benzene drying column, heavy-ends processing, the benzene recovery column, and MCB distillation (Vents B, C, D, E in Figure 5-13, respectively), equipment leak emissions, emissions from benzene storage, and secondary emissions from wastewater.<sup>19</sup>

Table 5-12 presents estimated controlled and uncontrolled emission factors for benzene emissions from the tail gas treatment vent, atmospheric distillation vents, equipment leak emissions, and benzene storage. The point source factors are based on emissions reported to EPA in response to information requests and trip reports. For information on emission factors for estimating equipment leak and storage tank emissions refer to Sections 4.5.2 and 4.5.3 respectively of this document. As noted in Table 5-12, carbon adsorption is an appropriate control technology for control of emissions from tail gas treatment and distillation column vents. The control technique applicable to process equipment leak emissions is an inspection/maintenance program for pumps, valves, and flanges. Internal floating roof tanks may be used to control benzene emissions resulting from benzene storage.

TABLE 5-12. EMISSION FACTORS FOR CHLOROBENZENE PRODUCTION BY DIRECT CHLORINATION OF BENZENE

SCC and Description	Emissions Source	Contol Device	Emission Factor in lb/ton (kg/Mg) <sup>a,b</sup>	Factor Rating
3-01-301-01 Chlorobenzene	Tail-gas Scrubber Treatment	Carbon Adsorption	0.0134 (0.0067)	U
Manufacturing - Tail-gas Scrubber		Uncontrolled	1.04 (0.52)	U
3-01-301-02 Chlorobenzene	Atmospheric Distillation Vents <sup>c</sup>	Carbon Adsorption	0.0084 (0.0042)	U
Manufacturing - Benzene Dry Distillation		Uncontrolled	0.64 (0.32)	U
3-01-301-04 Chlorobenzene Manufacturing - Heavy Ends Processing				
-01-301-05 Chlorobenzene Manufacturing - Monochlorobenzene Distillation				
-01-301-03 Chlorobenzene	Atmospheric Distillation Vent - Benzene Recovery	Carbon Adsorption	0.00104 (0.00052)	U
Manufacturing - Benzene Recovery		Uncontrolled	0.08 (0.04)	U
3-01-3-1080 Chlorobenzene Manufacturing - Equipment Leaks	Equipment Leaks	Detection and Repair of Major Leaks	See Section 4.5.2	
		Uncontrolled	See Section 4.5.2	

(continued)

TABLE 5-12. CONTINUED

SCC and Description	Emissions Source	Contol Device	Emission Factor in lb/ton (kg/Mg) <sup>a,b</sup>	Factor Rating
4-07-196-01 Organic Chemical	Benzene Storage Vessel	Internal Floating Roof	See Section 4.5.3	
Storage - Benzene Storage		Uncontrolled	See Section 4.5.3	

Source: Reference 19.

Emission factors are expressed as lb (kg) benzene emitted per ton (Mg) chlorobenzene product produced.
 These emission factors are based on a hypothetical plant producing 74,956 tons (68 Gg) monochlorobenzene, 13,669 tons (12.4 Gg) o-dichlorobenzene, and 17,196 tons (15.6 Gg) p-dichlorobenzene. The reader is urged to contact a specific plant as to process, products made, and control techniques used before applying these emission factors.

<sup>&</sup>lt;sup>c</sup> Includes the following vents: benzene dry distillation, heavy ends processing, and monochlorobenzene distillation.

### 5.8 LINEAR ALKYLBENZENE PRODUCTION

Approximately 2 percent of the benzene produced in the United States is used in the production of linear alkylbenzene (LAB). LAB (or linear alkylate) improves the surfactant performance of detergents. The primary end use for LAB is in the production of linear alkylbenzene sulfonates (LAS). Because of their water-soluble properties, LAS are used extensively in powdered home laundry products (over 50 percent of LAS produced) and in heavy-duty liquid products.<sup>99</sup>

Alkyl benzene sulfonates with highly branched C<sub>12</sub> side chains possess excellent detergent properties, and they have also been used in the past in formulating detergents. However, in recent years, LAS have essentially replaced all branched alkylbenzene sulfonates in detergent formulations in the United States because of environmental considerations. LAB is extensively degraded (>90 percent) by microorganisms in sewage plants after a relatively short period of time. In comparison, the highly branched alkyl benzene sulfonates have a much lower biological degradability. <sup>100</sup> Dodecylbenzene and tridecylbenzene are the two most common LABs. The locations of the LAB producers in the United States are shown in Table 5-13. <sup>11,101</sup>

In the United States, LAB is produced using two different processes. Vista's Baltimore plant uses a monochloroparaffin LAB production process. Vista's Lake Charles plant and Monsanto's Alvin plant use an olefin process, wherein hydrogen fluoride serves as a catalyst. Approximately 64 percent of LAB is produced by the olefin process. The paraffin chlorination process accounts for about 36 percent of LAB production. Both processes are described in the following sections.

### 5.8.1 Process Description for Production of LAB Using the Olefin Process

Production of LAB using the olefin process consists of two steps: a dehydrogenation reaction and an alkylation reaction. The  $C_{10}$  to  $C_{14}$  linear paraffins are

TABLE 5-13. U.S. PRODUCERS OF LINEAR ALKYLBENZENE (DETERGENT ALKYLATES)

		Annual Capacity million lb/yr	
Company	Location	(million kg/yr)	Process
Linear Alkylbenzene (Dodecyclbenzene and tridecyclbenz	ene)		
Monsanto Company Chemical Group	Alvin, TX	330 (150)	Internal olefinsHFl; merchant
Vista Chemical Company	Baltimore, MD	300 (140)	Monochloroparaffin, merchant and captive
	Lake Charles, LA	210 (95)	Internal olefinsHFl; merchant and captive
Linear Alkylbenzene (except dodecyl and tridecyl)			
Phillips 66 Company	NA	NA	
TOTAL		840 (385)	

Source: References 11 and 101.

NA = Not available

Note: This is a list of major facility that produce linear alkylbenzene. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel. These data for producers and locations were current as of January 1993.

dehydrogenated to n-olefins, which are reacted with benzene under the influence of a solid, heterogenous catalyst (such as hydrogen fluoride [HFI]) to form LAB. The discussion of LAB production using the olefin process is taken from references 102 and 103.

First, n-paraffins are transferred from bulk storage to the linear paraffin feed tank in Stream 1 (Figure 5-15.)<sup>103</sup> The paraffins are heated to the point of vaporization (Stream 2) and passed through a catalyst bed in the Pacol reactor (Stream 3), where the feed is dehydrogenated to form the corresponding linear olefins by the following reaction:

$$R_1 - CH_2 - CH_2 - R_2 - R_1 - CH = CH - R_2 + H_2$$

The resulting olefins contain from 10 to 30 percent  $\alpha$ -olefins, and a mixture of internal olefins, unreacted paraffins, some diolefins, and lower-molecular-weight "cracked materials." The gas mixture is quickly quenched with a cold liquid stream as it exits to process thermally-promoted side reactions (Stream 4). The hydrogen-rich offgases (e.g., hydrogen, methane, ethane, etc.) are then separated from the olefin liquid phases (Stream 5). The gas is used as process fuel (Stream 6) or vented to a flare stack.

Di-olefins in the Pacol separator liquid are selectively converted back to mono-olefins in the Define reactor (Stream 7). The effluent from the reactor is routed to a stripper (Stream 8), where light ends are removed (Stream 9). The olefin-paraffin mixture (Stream 10) is then alkylated with benzene (Stream 11) in the fixed-bed reactor to be blended with a HFl catalyst. The blend is held at reaction conditions long enough for the alkylation reaction to go to completion as follows:

$$R_1CH = CHR_2 + C_6H_6 ---> R_1CH_2 - CHR_2$$

Product from the reactor flows to the benzene stripping column (Stream 12) for separation and recycle of unreacted benzene to the fixed-bed reactor (Stream 13). The liquid HFl is also separated and recycled to the alkylation vessel to be mixed with fresh HFl.

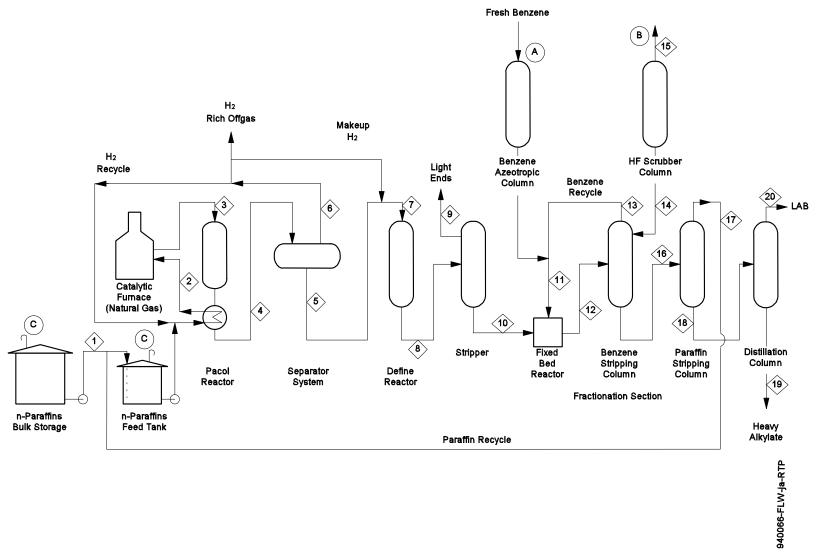


Figure 5-15. Linear Alkybenzene Production Using the Olefin Process

Source: Reference 103.

Following benzene stripping, a lime water solution is then fed into the HFl scrubber column (Stream 14) to neutralize the HFl. The solution is filtered (Stream 15); the wastewater is routed to the treatment facility and the solids are transferred to a landfill. Unreacted paraffins are separated in the paraffin stripping column (Stream 16) and recycled to the Pacol reactor (Stream 17). The last distillation column purifies the main LAB (Stream 18). Heavy alkylate byproducts are stored (Stream 19) and the pure LAB is transferred to storage tanks (Stream 20) awaiting sale.

### 5.8.2 Benzene Emissions from LAB Production Using the Olefin Process

Benzene emissions from the LAB olefin process are shown in Table 5-14. 102

The two major sources of emissions are the benzene azeotropic column (Vent A) and the HFl scrubber column controlling emissions from the benzene stripping column (Vent B). Some benzene can be emitted through the HFl scrubber column. Inert gases and air venting from the unit, temperature, and purge rate of the scrubber can influence the amount of volatiles emitted. These gases are usually sent to a flare. The control for both of these emissions is use as fuel. Benzene emissions can also occur from benzene storage tanks and equipment leaks. Refer to Section 4.5 for a discussion of benzene emissions from these sources.

### 5.8.3 <u>Process Description for Production of LAB Using the Chlorination Process</u>

The LAB chlorination process consists of two sequential reactions. In the first step, n-paraffins are chlorinated to monochlorinated n-paraffins. In the second reaction, benzene and crude secondary alkyl chlorides (chloroparaffins) are blended with an aluminum chloride catalyst to form crude LAB. The following discussion of LAB production using the chlorination process is taken from references 100 and 102.

As shown in Figure 5-16, n-paraffins (alkanes) (Stream 1) are reacted with liquid chlorine (Stream 2) in a series of UV-catalyzed chlorination reactors. The n-paraffins

TABLE 5-14. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL LINEAR ALKYLBENZENE PLANT USING THE OLEFIN PROCESS

SCC and Description	Emissions Source	Control Device	Emission Factor lb/ton (g/Mg) <sup>a,b</sup>	Factor Rating
3-01-211-02	Benzene Azeotropic	Uncontrolled	$7.4 \times 10^{-3} (3.7)$	U
Linear Alkylbenzene - Benzene Drying	Column Vent (Point A) <sup>c</sup>	Used as fuel	1.5 x 10 <sup>-6</sup> (7.4 x 10 <sup>-4</sup> )	U
3-01-211-03	Hydrogen Fluoride	Uncontrolled	0.022 (11)	U
Linear Alkylbenzene HFl Scrubber Vent	Scrubber Column Vent (Point B) <sup>c</sup>	Used as fuel	$4.4 \times 10^{-6} (2.2 \times 10^{-3})$	U
Seraccer vent	(1 ont <i>B</i> )	Flare	$2.2 \times 10^{-3} (1.1)$	U

Source: Reference 102.

Any given LAB olefin producing plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact Note: plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Emission factor estimates based on a 198 million lb/yr (90,000 Mg/yr) hypothetical plant.
 Emission factors refer to lb (g) benzene emitted per ton (Mg) LAB produced by the olefin process.

<sup>&</sup>lt;sup>c</sup> Letters refer to vents designated in Figure 5-15.

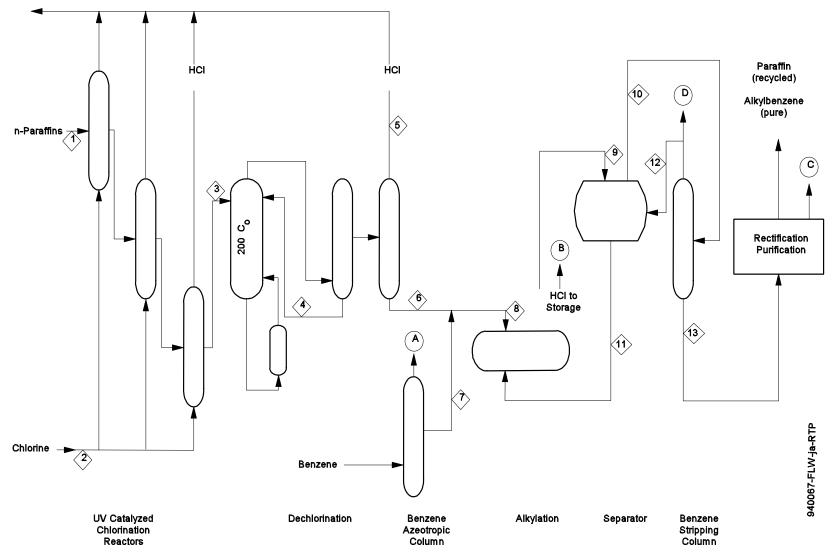


Figure 5-16. Production of Linear Alkybenzenes via Chlorination

Source: Reference 100.

are converted at 212°F (100°C) to a mixture of about 35 percent chlorinated paraffins, and the remainder to paraffins and HCl as shown in the following reaction:

$$R_1$$
 -  $CH_2$  -  $R_2$  +  $Cl$  --->  $R$  -  $CH$  -  $R_2$  +  $HCl$  + heat  $\mid$   $Cl$ 

Following this reaction, dehydrochlorination (elimination of HCl) of the monochloroalkanes takes place at 392 to 752°F (200 to 300°C) over an iron catalyst to form olefins (linear alkenes with internal double bonds) (Stream 3). It is necessary to remove all chlorinated paraffins (such as dichloroalkenes) from the process stream because they form other products besides LAB. Therefore, the remaining chlorinated paraffins are dehydrochlorinated to give tar-like products that are easily separated and recycled back to the reactor (Stream 4). HCl is also removed from the mixture (Stream 5), leaving a mixture of only olefins and paraffins for the alkylation reaction. <sup>100</sup>

This olefin-paraffin mixture (Stream 6) is combined with benzene from storage that has been dried in a benzene azeotropic column (Stream 7). These two streams are combined in an alkylation reactor with an aluminum chloride catalyst at 122°F (50°C) (Stream 8). The subsequent reaction produces LAB, illustrated below:

$$R_1$$
 -  $CH$  -  $R_2$  +  $C_6H_6$  --->  $R_1$  -  $CH$  -  $R_2$  +  $HCl$  + heat, possible olefins, 
$$| \\$$
 short-chained paraffins, etc.  $Cl$ 

At this point, HCl gas and some fugitive volatile organics given off during the reaction are treated with adsorbers and excess HCl is routed to storage (Vent B). Next, the LAB (Stream 9) is routed to a separator where hydrolysis is performed in the presence of HFl at 50°F (10°C) to separate crude LAB and the organics (benzene, tar, etc.) (Stream 10) from the catalyst sludge (Stream 11). Benzene is recovered in the benzene stripping column and recycled back to the reactor (Stream 12).

The resulting paraffin-alkylate mixture (Stream 13) is sent through rectification and purification (which includes washing and decanting) to yield pure alkylbenzene and paraffin, which can be recycled as feedstock. 100

# 5.8.4 <u>Benzene Emissions from LAB Production Using the Chlorination Process</u>

Benzene emissions using the LAB chlorination process are shown in Table 5-14. The four major points of benzene emissions are listed below. Emission factors for these points also are presented in Table 5-15.<sup>102</sup>

One emission point is the benzene azeotropic column vent, which serves to dry the benzene before it enters the alkylation reactor. Some benzene emissions can escape from the vent in the column (Vent A). The quantity of escaping emissions is dependent on the dryness of the benzene and the design of the column condenser.

A second emission point is the hydrochloric acid adsorber vent. Following the alkylation reaction, the HCl gas and fugitive volatile organics are treated by absorbers. Most of the product goes to hydrochloric acid storage, but some is vented off (Vent B). The amount of benzene emissions given off here is dependent on the fluid temperature in the absorber and the vapor pressure of the mixed absorber fluid.

The third type of emission point is the atmospheric wash decanter vents. In the final purification/rectification stage, the crude LAB is washed with alkaline water to neutralize it. Benzene emissions can escape from these atmospheric washer vents (Vent C).

Finally, in the benzene stripping column, benzene is recovered and returned to the benzene feed tank. Residual inert gases and benzene emissions can occur at this point (Vent D). The amount of benzene in the stream depends on the quantity of inert gases and the temperature and design of the reflux condenser used.

TABLE 5-15. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL LINEAR ALKYLBENZENE PLANT USING THE CHLORINATION PROCESS

SCC and Description	Emissions Source	Control Device	Emission Factor in lb/ton (g/Mg) <sup>a</sup>	Factor Rating
3-01-211-02	Benzene Azeotropic	Uncontrolled	$7.4 \times 10^{-3} (3.7)$	U
Linear Alkylbenzene-Benzene Drying	Column Vent (Point A) <sup>c</sup>	Used as fuel	$1.5 \times 10^{-6} (7.4 \times 10^{-4})$	U
3-01-211-23	Hydrochloric Acid	Uncontrolled	0.5 (250)	U
Linear Alkylbenzene - HCl Adsorber Vent	Adsorber Vent (Point B) <sup>c</sup>	Used as fuel	1 x 10 <sup>-4</sup> (0.05)	U
3-01-211-24	Atmospheric	Uncontrolled	0.0246 (12.3)	U
Linear Alkylbenzene - Atmospheric Wash/Decanter Vent	Wash/Decanter Vent (Point C) <sup>c</sup>	Used as a fuel	5 x 10 <sup>-6</sup> (2.5 x 10 <sup>-3</sup> )	U
3-01-211-25	Benzene Stripping Column	Uncontrolled	$7.4 \times 10^{-3} (3.7)$	U
Linear Alkylbenzene - Benzene Strip Column	Vent (Point D) <sup>c</sup>	Used as a fuel	1.48 x 10 <sup>-6</sup> (7.4 x 10 <sup>-4</sup> )	U

Source: Reference 102.

Note: Any given LAB olefin producing plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

<sup>&</sup>lt;sup>a</sup> Emission factor estimates based on a 198 million lb/yr (90,000 Mg/yr) hypothetical plant.

Emission factors refer to lb (g) benzene emitted per ton (Mg) LAB produced by the chlorination process.

Letters refer to vents designated in Figure 5-16.

The most frequently applied control option for all of these sources is to use the emissions for fuel.

### 5.9 OTHER ORGANIC CHEMICAL PRODUCTION

Several additional organic chemicals that are produced using benzene as a feedstock are believed to have benzene emissions. These chemicals include hydroquinone, benzene sulfonic acid, resorcinol, biphenyl, and anthraquinone. A brief summary of the producers, end uses, and manufacturing processes for these chemicals is given below. No emissions data were available for these processes.

# 5.9.1 <u>Hydroquinone</u>

The primary end use of hydroquinone is in developing black-and-white photographic film (46 percent). A secondary end use is as a raw material for rubber antioxidants (31 percent). <sup>104</sup>

A technical grade of hydroquinone is manufactured using benzene and propylene as raw materials by Goodyear Tire and Rubber Company in Bayport, TX, 11 million lb/yr (5 million kg/yr) and by the Eastman Chemical Company, Tennessee Eastman Division, in Kingsport, Tennessee, 26 million lb/yr (12 million kg/yr). 11,101

In this process, benzene and recycled cumene are alkylated with propylene in the liquid phase over a fixed-bed silica-alumina catalyst to form a mixture of diisopropylbenzene isomers. The meta isomer is transalkylated with benzene over a fixed bed silica-alumina catalyst to produce cumene for recycle. The para isomer is hydroperoxidized in the liquid phase, using gaseous oxygen, to a mixture of diisopropylbenzene hydroperoxide isomers. The mono isomer is recycled to the hydroperoxidation reactor. The diisopropylbenzene hydroperoxide is cleaved in the liquid phase with sulfuric acid to hydroquinone and acetone. Acetone is produced as a co-product. 104

## 5.9.2 <u>Benzophenone</u>

Benzophenone (diphenylketone) is used as an intermediate in organic synthesis, and as an odor fixative. Derivatives are used as ultraviolet (UV) absorbers, such as in the UV curing of inks and coatings. <sup>105</sup> Benzophenone is also used as flavoring, soap fragrance, in pharmaceuticals, and as a polymerization inhibitor for styrene. Nickstadt-Moeller, Inc., in Ridgefield, New Jersey, and PMC, Inc., PMC Specialties Group Division in Chicago, Illinois, produce a technical grade of benzophenone. <sup>11</sup> Benzophenone is also produced by Upjohn Company, Fine Chemicals. <sup>101</sup> Benzophenone is produced by acylation of benzene and benzyl chloride. <sup>68</sup>

# 5.9.3 Benzene Sulfonic Acid

Benzene sulfonic acid is used as a catalyst for furan and phenolic resins and as a chemical intermediate in various organic syntheses including the manufacture of phenol and resorcinol. Benzene sulfonic acid is manufactured by sulfonation--reacting benzene with fuming sulfuric acid. Burroughs Wellcome in Greenville, North Carolina; CL Industries, Inc., in Georgetown, Illinois; and Sloss Industries Corporation in Birmingham, Alabama, produce benzene sulfonic acid. 11

### 5.9.4 Resorcinol

Resorcinol is produced by INDSPEC Chemical Corporation in Petrolia,
Pennsylvania. Resorcinol is produced by fusing benzene-m-disulfonic acid with sodium hydroxide. Resorcinol is used in manufacturing resorcinol-formaldehyde resins, dyes, and pharmaceuticals. It is also used as a cross-linking agent for neoprene, as a rubber tackifier, in adhesives for wood veneers and runner-to-textiles composites, and in the manufacture of styphnic acid and cosmetics. 106

## 5.9.5 <u>Biphenyl</u>

Biphenyl (diphenyl or phenylbenzene) is produced by Chemol Co. in Greensboro, North Carolina; Koch Refining Co. in Corpus Christi, Texas; Monsanto Co. in Anniston, Alabama; Sybron Chemical Inc., in Wellford, South Carolina; and Chevron Chemical Co. of Chevron Corp. 11,101 One method for producing biphenyl is by dehydrogenation--slowly passing benzene through a red-hot iron tube. 106

Biphenyl is used in organic synthesis, as a heat-transfer agent, as a fungistat in packaging citrus fruit, in plant disease control, in the manufacture of benzidine, and as a dyeing assistant for polyesters. <sup>106</sup> In 1991, 8,976 tons (8,143 Mg) of biphenyl were sold. <sup>101</sup>

# 5.9.6 <u>Anthraquinone</u>

Anthraquinone is manufactured by heating phthalic anhydride and benzene in the presence of aluminum chloride and dehydrating the product. Anthraquinone is used as an intermediate for dyes and organics, as an organic inhibitor, and as a bird repellent for seeds.

### 5.10 BENZENE USE AS A SOLVENT

Benzene has been used historically as an industrial solvent. Because benzene is readily soluble in a variety of chemicals (including alcohol, ether, and acetone), it has commonly been used as an agent to dissolve other substances. As an industrial solvent, benzene application has included use as an azeotropic agent, distilling agent, reaction solvent, extracting solvent, and recrystallizing agent. However, benzene use as an industrial solvent has been steadily declining over the last few years because of its adverse health effects and increased regulation. The Occupational Safety and Health Administration has cited health risk to workers from exposure to benzene, and EPA has classified benzene as a Group A chemical, a known human carcinogen. <sup>107</sup>

Source categories that currently use benzene as a solvent include pharmaceutical manufacturing; general organic synthesis; alcohol manufacturing; caprolactam production, and plastics, resins, and synthetic rubber manufacturing. Benzene is also used in small quantities (generally less than 0.1 percent) in solvents used in the rubber tire manufacturing industry; however, the amount of emissions generated is variable depending on the amount of solvent used. <sup>108</sup>

Facilities in the above-listed source categories indicate that they plan to eliminate benzene solvent use in the next few years. Facilities have been experimenting with substitutes, such as toluene, cyclohexane, and monochlorobenzene. However, those facilities that continue to use benzene indicate that they have been unable to identify a solvent substitute as effective as benzene. Facilities in the above-listed source categories indicate that they plan to eliminate benzene experimenting with substitutes, such as toluene, cyclohexane, and monochlorobenzene. However, those facilities that continue to use benzene indicate that they have been unable to identify a solvent substitute as effective as benzene.

Several facilities in the source categories listed above reported benzene emissions in the 1992 TRI. These facilities and their locations are included in Table 5-16.

Emissions of benzene from solvent used in the manufacture and use of pesticides, use of printing inks, application of surface coatings, and manufacture of paints are believed to be on the decline or discontinued. However, several facilities in these source categories reported benzene emissions in the 1992 TRI. These facilities and their locations are also included in Table 5-16.

Benzene continues to be used in alcohol manufacture as a denaturant for ethyl alcohol. It is also used as an azeotropic agent for dehydration of 95 percent ethanol and 91 percent isoproponal. Companies currently producing these alcohols are presented in Table 5-17. Table 5-17.

Benzene is also used as a solvent to extract crude caprolactam. The three major caprolactam facilities currently operating in the United States are listed in

TABLE 5-16. PARTIAL LIST OF MANUFACTURERS IN SOURCE CATEGORIES WHERE BENZENE IS USED AS A SOLVENT

Solvent Use Source Category	Location
Plastics Materials and Resins	
Amoco Chemical Co.	Moundville, AL
Arizona Chemical Co.	Gulfport, MS
Chemfax Inc.	Gulfport, MS
Exxon Chemical Americas Baton	Baton Rouge, LA
Rouge Resin Finishing	<i>5</i> ,
Formosa Plastics Corp.	Point Comfort, TX
Lawter Intl. Inc.	Moundville, AL
Southern Resin Division	•
Neville Chemical Co.	Pittsburgh, PA
Quantum Chemical Corp. La Porte	La Porte, TX
Quantum Chemical Corp.	Clinton, IA
USI Division	
Rexene Corp. Polypropylene Plant	Odessa, TX
Union Carbide Chemicals & Plastics	Texas City, TX
Co. Texas City Plant	·
Pharmaceutical Manufacturing	
Warner-Lambert Co.	
Parke Davis Division	Holland, MI
Pesticides and Agricultural Chemicals	
Rhone-Poulenc Ag Co.	Institute, WV
Agribusiness Maketers, Inc.	Baton Rouge, LA
Commercial Printing (Gravure)	
Piedmont Converting, Inc.	Lexington, NC

(continued)

TABLE 5-16. CONTINUED

Solvent Use Source Category	Location
Paints and Allied Products	
BASF Corporation Inks & Coating Division	Greenville, OH
St. Louis Paint Manufacturing Co., Inc.	St. Louis, MS
Synthetic Rubber	
DuPont Pontchartrain Works	La Place, LA
DuPont Beaumont Plant	Beaumont, TX

Source: Reference 111.

TABLE 5-17. U.S. PRODUCERS OF ETHANOL OR ISOPROPANOL

Facility	Location	Annual Capacity million gal (million L)
thanol		
Archer Daniels Midland Company ADM Corn Processing Division	Cedar Rapids, IA Clinton, IA Decatur, IL Peoria, IL Walhalla, ND	700 (2,650) 11 (42)
Biocom USA Ltd.	Jennings, LA	40 (151)
Cargill, Incorporated Domestic Corn Milling Division	Eddyville, IA	30 (113)
Chief Ethanol Fuels Inc.	Hastings, NB	14 (53)
Eastman Chemical Company Texas Eastman Division	Longview, TX	25 (95)
Georgia-Pacific Corporation Chemical Division	Bellingham, WA	12 (45)
Giant Refining Co.	Portales, NM	10 (38)
Grain Processing Corporation	Muscatine, IA	60 (227)
High Plains Corp.	Colwich, KS	15 (57)
Hubinger-Roquette Americas, Inc.	Keokuk, IA	11 (42)
Midwest Grain Products, Inc.	Atchison, KS Pekin, IL	22 (83) 19 (72)
Minnesota Corn Processors	Columbus, NB Marshall, MN	NA 28 (106)
New Energy Company of Indiana	South Bend, IN	70 (265)
Pekin Energy Company	Pekin, IL	80 (303)
Quantum Chemical Corp. USI Division	Tuscola, IL	68 (257)
South Point Ethanol	South Point, OH	60 (227)
A. E. Staley Manufacturing Company Sweetner Business Group Ethanol Division	Loudon, TN	60 (227)

(continued)

TABLE 5-17. CONTINUED

Facility	Location	Annual Capacity million gal (million L)
Ethanol (continued)		
Union Carbide Corporation Solvents and Coatings Materials Division	Texas City, TX	123 (466)
	TOTAL	1,458 (5,519)
Isopropanol		
Exxon Chemical Company Exxon Chemical Americas	Baton Rouge, LA	650 (2,460)
Lyondell Petrochemical Company Shell Chemical Company	Channelview, TX Deer Park, TX	65 (246) 600 (2,271)
Union Carbide Corporation Solvents and Coatings Materials Division	Texas City, TX	530 (2,006)
	TOTAL	1,845 (6,984)

Source: References 11 and 111.

NA = Not available

-- = no emissions reported

<sup>&</sup>lt;sup>a</sup> Emissions listed are those reported in the 1992 TRI.

Table 5-18.<sup>11,111</sup> Of the three facilities, DSM and BASF use benzene as a solvent, and Allied Signal produces benzene as a co-product.<sup>113</sup>

Benzene is also used as a solvent in the blending and shipping of aluminum alkyls. 113

Emission points identified for solvent benzene are process vents, dryer vents, and building ventilation systems.<sup>107</sup> As shown in Table 5-19, only one emission factor was identified for any of the solvent use categories.<sup>114</sup> The emission factor presented is for the vacuum dryer vent controlled with a venturi scrubber in pharmaceutical manufacturing.

TABLE 5-18. U.S. PRODUCERS OF CAPROLACTAM

Facility	Location	Annual Capacity million lb (million kg)	Raw Material
Allied-Signal, Inc. Engineered Materials Sector	Hopewell, VA	660 (299)	Phenol
BASF Corporation Chemicals Division Fiber Raw Materials	Freeport, TX	420 (191)	Cyclohexane
DSM Chemicals North America, Inc.	August, GA	360 (163)	Cyclohexane
	TOTAL	1,440 (653)	

Source: References 11 and 111.

<sup>&</sup>lt;sup>a</sup> Emissions listed are those reported in the 1992 TRI.

<sup>&</sup>quot;--" = no emissions reported.

TABLE 5-19. SUMMARY OF EMISSION FACTORS FOR BENZENE USE AS A SOLVENT

SCC and Description	Emissions Source	Control Device	Emission Factor <sup>a</sup> lb/1,000 gal (g/L)	Factor Rating
3-01-060-01 Pharmaceuticals - General Process - Vacuum Dryers	Vacuum Dryer Vent	Venturi Scrubber (99.10% efficiency)	2.1 (0.25)	В

Source: Reference 114.

<sup>&</sup>lt;sup>a</sup> Factor is expressed as lb (kg) benzene emitted per 1,000 gal (L) pharmaceutical product produced.